

## PATENT ABSTRACTS OF JAPAN

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### (54) ADDITIVE FOR PAPERMAKING

#### (57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain an additive for papermaking having a comparatively low viscosity and a good handleability in a high concentration, and excellent in various properties as the additive for the papermaking by including a (meth) acrylamide-based copolymer highly polymerized without gelation.

**SOLUTION:** This additive for papermaking comprises (A) a (meth)acrylamide, (B) a monomer having one (meth) allyl group as a carbon to carbon double bond, (C) an N-substituted (meth)acrylamide of the formula  $\text{CH}_2=\text{C}(\text{R}_1)-\text{CONR}_2(\text{R}_3)$  ( $\text{R}_1$  is H or methyl;  $\text{R}_2$  is H or a 1-4C straight or branched alkyl;  $\text{R}_3$  is a 1-4C straight or branched alkyl) and (D) a (meth)acrylamide-based copolymer obtained by copolymerizing a polyfunctional monomer.

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**CLAIMS**

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**[Claim(s)]**

[Claim 1] (A) (meta) Acrylamide, the monomer which has one allyl group as a (B) carbon-carbon double bond (meta), (C) General formula (1): $\text{CH}_2 = \text{C}(\text{R}1)-\text{CONR}2$  (among a formula (R3)) R1 A hydrogen atom or a methyl group, and R2 The straight chain of a hydrogen atom or carbon numbers 1-4, or the alkyl group of branched chain, R3 the alkyl group of the straight chain of carbon numbers 1-4, or branched chain -- expressing -- additive for paper manufacture which comes to contain N-permutation (meta) acrylamides expressed and the acrylamide system copolymer obtained by copolymerizing (D) polyfunctional monomer (meta).

[Claim 2] (A) (meta) Monomer [ which has one allyl group as a (B) carbon-carbon double bond (meta) acrylamide 99.899 - 79.9 mol% ] 0.05 - ten-mol %, (C) General formula (1): $\text{CH}_2 = \text{C}(\text{R}1)-\text{CONR}2$  (among a formula (R3)) R1 A hydrogen atom or a methyl group, and R2 The straight chain of a hydrogen atom or carbon numbers 1-4, or the alkyl group of branched chain, R3 the alkyl group of the straight chain of carbon numbers 1-4, or branched chain -- expressing -- 0.05-10-mol % of N-permutation (meta) acrylamides expressed -- And the additive for paper manufacture which comes to contain the acrylamide system copolymer obtained by copolymerizing (D) polyfunctional monomer 0.001 - 0.1-mol % (meta).

[Claim 3] (A) (meta) Acrylamide, the monomer which has one allyl group as a (B) carbon-carbon double bond (meta), (C) General formula (1): $\text{CH}_2 = \text{C}(\text{R}1)-\text{CONR}2$  (among a formula (R3)) R1 A hydrogen atom or a methyl group, and R2 The straight chain of a hydrogen atom or carbon numbers 1-4, or the alkyl group of branched chain, R3 the alkyl group of the straight chain of carbon numbers 1-4, or branched chain -- expressing -- N-permutation (meta) acrylamides expressed -- (D) A polyfunctional monomer and the anionic vinyl monomer except a (E) (aforementioned A) - (C) component, The additive for paper manufacture which comes to contain the acrylamide system copolymer obtained by copolymerizing at least one sort chosen from a cationic vinyl monomer and a nonionic vinyl monomer (meta).

[Claim 4] (A) (meta) Monomer 0.05 - ten-mol % and (C) general formula (1): $\text{CH}_2 = \text{C}(\text{R}1)-\text{CONR}2$  (among a formula (R3)) which has one allyl group as a (B) carbon-carbon double bond (meta) acrylamide 99.899 - 55-mol% R1 A hydrogen atom or a methyl group, and R2 The straight chain of a hydrogen atom or carbon numbers 1-4, or the alkyl group of branched chain, R3 the alkyl group of the straight chain of carbon numbers 1-4, or branched chain -- expressing -- 0.05-10-mol % of N-permutation (meta) acrylamides expressed -- (D) The anionic vinyl monomer except a polyfunctional monomer 0.001 - 0.1-mol % and (E) (aforementioned A) - (C) component, The additive for paper manufacture which comes to contain the acrylamide system copolymer which is chosen from a cationic vinyl monomer and a nonionic vinyl monomer, and which is obtained by copolymerizing less than [ 1 sort 40 mol % ] at least (meta).

[Claim 5] (B) The additive for paper manufacture according to claim 1 to 4 whose monomer which has one allyl group as a carbon-carbon double bond (meta) is at least one sort chosen from an allyl compound (meta) carboxylic acid, allyl compound (meta) sulfonic acids, these salts, and (meta) allyl alcohol.

[Claim 6] (C) The additive for paper manufacture according to claim 1 to 4 whose N-permutation (meta) acrylamides are at least one sort chosen from N and N-dimethyl (meta) acrylamide, N-methyl (meta) acrylamide, N-ethyl (meta) acrylamide, N-isopropyl (meta) acrylamide, and N-t-butyl (meta)

acrylamide.

[Claim 7] (E) as a component -- the total mol sum of all monomers -- receiving -- an anionic vinyl monomer -- a 1-15-mol % and cationic vinyl monomer -- 1-15-mol % -- the additive for paper manufacture according to claim 3 or 4 which it comes to use.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]**

[0001]

[Field of the Invention] This invention relates to the additive for paper manufacture. In detail, it is related with the additive for paper manufacture which comes to contain the acrylamide (meta) system copolymer of high branching structure.

[0002]

[Description of the Prior Art] In recent years, on the occasion of manufacture of paper and the paper board, importance has been attached to the additive for paper manufacture, especially the paper reinforcing agent. It is further raised with the purpose of energy saving or saving resources that use of good pulp was restricted with aggravation of a bolt supply situation as this background and that the need for reuse of used paper became strong much more, and the additive for paper manufacture as a modifier of paper and the paper board is much more indispensable as that result.

[0003] On the other hand, the dependence and its use range of a filtration improvement agent and a paper reinforcing agent have spread further for the purpose of upgrading according to the improvement in the productivity accompanying improvement in the speed of a paper machine, or diversification of paper. As an additive for paper manufacture, a polyacrylamide system is in use under this situation.

[0004] however, conventionally well-known in recent years, since the service condition of the additive for paper manufacture is becoming still severer -- it is coming to the limitation by the additive for polyacrylamide system paper manufacture of low molecular weight in respect of the effectiveness as an additive comparatively. Therefore, the means of macromolecule quantification is taken in order to aim at improvement in the engine performance, but since the viscosity of the copolymer obtained rises too much when macromolecule quantification is only carried out, the dispersibility at the time of paper making serves as a defect. Consequently, when this copolymer is used as an additive for paper manufacture, too much condensation arises, and it is easy to cause the conditions turbulence of perfect paper. Moreover, the high-concentration product (additive for paper manufacture) is demanded from reduction of transportation cost, and the field of improvement in productivity.

[0005] That these troubles should be canceled, branching structure is given by using a polyfunctional vinyl monomer (what has at least two double bonds), and the attempt to which you are going to make it increase the molecular weight is made, suppressing a viscosity rise of the copolymer obtained. For example, Uono and others (JP,53-114911,A) has proposed using divinyl system monomers, such as methylenebis acrylamide, as a cross linking agent component. However, Uono and others has also pointed out gelling, if the addition of a divinyl system monomer is increased to coincidence. This is in agreement with the theory (Principles of Polymer Sciense, Cornell University Press IthacaN.Y., 1953) of gelation by the system which added the divinyl system monomer which Flory pointed out. Moreover, although Kimura and others recommended 3 organic-functions vinyl monomer (JP,2-61197,A), according to recognition of this invention person or the experiment fact, the gelation effectiveness same as the above is only amplified, and it resulted in making manufacture of the additive for paper manufacture more difficult compared with the case where a divinyl system monomer is used on the contrary. Moreover, when little use of the polyfunctional vinyl monomer was carried out, the polymer of the amount of macromolecules could not be obtained, and the

effectiveness as an additive for paper manufacture was not yet enough.

[0006] Moreover, the attempt which is going to give branching structure is also made by using the vinyl monomer which has chain transfer nature substituents, such as allyl compound (meta) acrylate and N,N-dimethylacrylamide, (JP,5-195485,A). However, when the vinyl monomer which has a chain transfer nature substituent is used, although gelation cannot take place easily, molecular weight distribution cannot become large and it cannot obtain the acrylamide (meta) system copolymer of the amount of macromolecules. This is pointed out by said Flory.

[0007]

[Problem(s) to be Solved by the Invention] Without being accompanied by gelation, this invention comes to contain the acrylamide (meta) system copolymer which carried out macromolecule quantification, and also in high concentration, handling nature is comparatively good at hypoviscosity, and it aims at offering the additive for paper manufacture which is moreover excellent in many engine performance as an additive for paper manufacture.

[0008]

[Means for Solving the Problem] As a result of repeating research wholeheartedly that this invention persons should solve the technical problem of said conventional technique, the acrylamide (meta) system copolymer of the specific presentation shown below came to complete a header and this invention for the ability of said purpose to be attained.

[0009] Namely, the monomer in which this invention has one allyl group as a (A) (meta) acrylamide and (B) carbon-carbon double bond (meta), (C) General formula (1): $\text{CH}_2 = \text{C}(\text{R}1)-\text{CONR}2$  (among a formula (R3)) R1 A hydrogen atom or a methyl group, and R2 The straight chain of a hydrogen atom or carbon numbers 1-4, or the alkyl group of branched chain, R3 the alkyl group of the straight chain of carbon numbers 1-4, or branched chain -- expressing -- it is related with the additive for paper manufacture which comes to contain N-permutation (meta) acrylamides expressed and the acrylamide system copolymer obtained by copolymerizing (D) polyfunctional monomer (meta). Furthermore, (A) (meta) acrylamide, the monomer which has one allyl group as a (B) carbon-carbon double bond (meta), (C) General formula (1): $\text{CH}_2 = \text{C}(\text{R}1)-\text{CONR}2$  (among a formula (R3)) R1 A hydrogen atom or a methyl group, and R2 The straight chain of a hydrogen atom or carbon numbers 1-4, or the alkyl group of branched chain, R3 the alkyl group of the straight chain of carbon numbers 1-4, or branched chain -- expressing -- N-permutation (meta) acrylamides expressed -- (D) A polyfunctional monomer and the anionic vinyl monomer except a (E) (aforementioned A) - (C) component, It is related with the additive for paper manufacture which comes to contain the acrylamide system copolymer obtained by copolymerizing at least one sort chosen from a cationic vinyl monomer and a nonionic vinyl monomer (meta).

[0010]

[Embodiment of the Invention] In this invention, (A) (meta) acrylamide means acrylamide or methacrylamide, it can be independent-used or these can be used together. It is good to carry out independent use of the acrylamide from the field of economical efficiency. in addition, following this invention -- setting (meta) -- it is the same semantics.

[0011] (B) The monomer which has one allyl group as a carbon-carbon double bond (meta) means the monomer which has one allyl group (meta) in a molecule, and does not have a carbon-carbon double bond other than an allyl group (meta). (Meta) An allyl group is a functional group which generally has chain transfer nature, and it is thought in this invention that it has the function of both a chain transfer agent and a cross linking agent. As a monomer which has one allyl group as such a (B) carbon-carbon double bond (meta), at least one sort chosen from an allyl compound (meta) sulfonic acid, allyl compound (meta) carboxylic acids, these salts, and (meta) allyl alcohol can be used. Also in these (B) components, an allyl compound (meta) sulfonic acid or its salt is desirable at the point in which the acrylamide system copolymer obtained (meta) carries out macromolecule quantification, and a meta-allyl compound sulfonic acid or its salt is more desirable from the stability of a monomer especially. In addition, as a salt, alkali-metal salts, such as sodium salt and potassium salt, ammonium salt, etc. are raised.

[0012] (C) general formula (1): $\text{CH}_2 = \text{C}(\text{R}1)-\text{CONR}2$  (R(R3) 1 -- a hydrogen atom or a methyl group --) R2 The straight chain of a hydrogen atom or carbon numbers 1-4, or the alkyl group of branched chain, R3 N-permutation (meta) acrylamides expressed with the alkyl group of the straight chain of

carbon numbers 1-4 or branched chain It is going to introduce much branching structure into the copolymer obtained by this using the methyl group or methylene group in N-alkyl group acting as a chain transfer point. If this technique is used, branched polymer without gelation can be obtained. R2 in said general formula (1) Or R3 With the alkyl group of the straight chain of carbon numbers 1-4 which can be set, or branched chain, a methyl group, an ethyl group, an isopropyl group, t-butyl, etc. are raised. (C) As an example of a component, N and N-dimethyl (meta) acrylamide, N-isopropyl (meta) acrylamide, N-methyl (meta) acrylamide, N-ethyl (meta) acrylamide, N-isopropyl (meta) acrylamide, and N-t-butyl (meta) acrylamide are raised, and at least one sort chosen from these can be used. N,N-dimethylacrylamide is desirable in respect of copolymeric and chain transfer nature also in these (C) components.

[0013] Moreover, that to which (D) polyfunctional monomer has at least two carbon-carbon double bonds in a molecule is said, and the following are raised as a typical thing. As a 2 functionality vinyl monomer, for example, ethylene GURIKORUJI (meta) acrylate, Di(meth)acrylate, such as diethylene GURIKORUJI (meta) acrylate and TORIECHIRENGURIKORUJI (meta) acrylate Methylenebis (meta) acrylamide, ethylene bis(meta) acrylamide, Bis(meta) acrylamides, such as hexa methylenebis (meta) acrylamide Divinyl ester [, such as an adipic-acid divinyl and a sebacic-acid divinyl ], allyl compound methacrylate, diaryl amine, diaryl dimethylammonium, diallyl phthalate, diallyl chlorendate, divinylbenzene, N, and N-diaryl acrylamide etc. is raised. moreover -- as 3 functionality monomer -- 1, 3, 5-thoria chestnut roil hexahydro-S-triazine, triallyl isocyanurate, a triaryl amine, triallyl trimellitate, etc. -- as 4 functionality vinyl monomer -- tetramethylolmethane tetraacrylate, tetra-allyl compound pyromellitate, N and N, N', and N' - tetra-allyl compound-1,4-diaminobutane, a tetra-allylamine salt, tetra-allyloxy ethane, etc. are raised. These are independent in a kind or can use two or more sorts. As a desirable example, 1, 3, 5-thoria chestnut roil hexahydro-S-triazine, triallyl isocyanurate, etc. are raised also in these (D) polyfunctional monomer.

[0014] This invention manufactures the acrylamide (meta) system copolymer which carried out macromolecule quantification by using the aforementioned (B) component, the (C) component, and the (D) component, without being accompanied by gelation. Namely, although it contributes to producing gelation and the branching reaction according to chain transfer only at the (B) component or the (C) component on the other hand only of the (D) component molecular weight distribution cannot become large and molecular weight cannot fully be raised -- further, even when [ with the (D) component, the (B) component, or the (C) component ] it combines it is difficult for molecular weight distribution to acquire the acrylamide (meta) system copolymer of the narrow amount of macromolecules -- rattlingly -- since -- molecular weight distribution manufacture the acrylamide (meta) system copolymer of the narrow amount of macromolecules combining all these (B) components, the (C) components, and (D) components. In addition, it replaces with the (B) component or the (C) component, and even if it combines chain transfer agents generally known, such as isopropyl alcohol, the molecular weight distribution of this invention cannot acquire the acrylamide (meta) system copolymer of the narrow amount of macromolecules.

[0015] this invention -- as the constituent of an acrylamide (meta) system copolymer -- the aforementioned (A) component, the (B) component, the (C) component, and the (D) component -- in addition, at least one sort chosen from the anionic vinyl monomer except the - (C) component (aforementioned [ A ]), a cationic vinyl monomer, and a nonionic vinyl monomer as a (E) component can be used further. Namely, what is necessary is just to use a cationic vinyl monomer, in what is necessary's being just to use an anionic vinyl monomer in giving anionic to the copolymer obtained and giving cationicity to the copolymer obtained. What is necessary is just to use both anionic vinyl monomer and cationic vinyl monomer, in giving anionic and cationicity to the copolymer obtained and making it both sexes. Moreover, it is used in order to give hydrophobicity to a polymer, and it can use together with the - (D) component (aforementioned [ A ]) independently, and also a nonionic vinyl monomer can also be used together combining said ionicity vinyl monomer.

[0016] As an anionic vinyl monomer in the aforementioned (E) component, alkali-metal salts, such as sodium salt of organic sulfonic-acids [, such as dicarboxylic acid; vinyl sulfonic acids, such as monocarboxylic acid; maleic acids, such as an acrylic acid and a crotonic acid, boletic acid, an itaconic acid, and muconic acid, a styrene sulfonic acid, and 2-acrylamido-2-methyl propane sulfonic

acid ]; or these various organic acids and potassium salt, ammonium salt, etc. are raised, for example (meta).

[0017] (E) As a cationic vinyl monomer in a component For example, dimethylaminoethyl (meta) acrylate, diethylaminoethyl (meta) acrylate, The vinyl monomers which have the third class amino groups, such as dimethylaminopropyl (meta) acrylamide and diethylamino propyl (meta) acrylamide, or those hydrochloric acids, The salts of inorganic acids, such as a sulfuric acid and an acetic acid, or an organic acid, or this the third class amino-group content vinyl monomer and methyl chloride, The vinyl monomer containing the quarternary ammonium salt obtained by the reaction with the fourth class-sized agents, such as benzyl chloride, a dimethyl sulfate, and epichlorohydrin, etc. is raised.

[0018] (E) As a nonionic vinyl monomer in a component, the alkyl ester (carbon numbers 1-8 of an alkyl group) of said anionic vinyl monomer, acrylonitrile, styrene, vinyl acetate, the methyl vinyl ether, etc. are raised.

[0019] In this invention, the amount of each [ used ] of each component of the copolymer which consists of a (A) - (D) component must be determined enough in consideration of the engine performance as an additive for paper manufacture of the copolymer obtained. namely, the (A) component -- the total mol sum of (A) - (D) component -- receiving -- usually -- about 99.899-79.9 mol % -- desirable -- 99.2 - 80-mol % -- it is 99.2 - 90-mol % more preferably. the case where the (E) component is used on the other hand -- the (A) component -- the total mol sum of (A) - (E) component -- receiving -- usually -- about 99.899-55 mol % -- it is 99.2 - 70-mol % preferably. In addition, when not filling the (A) component to 55-mol%, it is difficult to get in sufficient paper durability effectiveness as an additive for paper manufacture etc.

[0020] (B) a component -- the same -- the total mol sum of (A) - (D) component, or the total mol sum of (A) - (E) component -- receiving -- usually -- 0.05 - ten-mol % -- it is 0.1 - five-mol % preferably. (B) Since the effectiveness of chain transfer is small and generation of the branch point also has it when not filling a component to 0.05-mol%, branching structure is inadequate. [ little ] Since the effectiveness of chain transfer is too strong when exceeding ten-mol %, a polymer chain becomes short and it is hard coming to generate the amount polymer of macromolecules.

[0021] (C) a component -- the same -- said total mol sum -- receiving -- usually -- 0.05-10-mol % -- it is 0.1-5-mol % preferably. (C) Since there is little generation of the branch point when not filling a component to 0.05-mol%, branching structure is inadequate. In exceeding ten-mol %, there is an inclination for the branching reaction by chain transfer to increase and to cause gelation.

[0022] (D) a component -- the same -- said total mol sum -- receiving -- usually -- 0.001-0.1-mol % - - desirable -- 0.005-0.08-mol % -- it is 0.01-0.05-mol % more preferably. (D) A component shortens the production time of an acrylamide (meta) system copolymer, and makes manufacture easy while it carries out macromolecule quantification of the acrylamide system copolymer, without being accompanied by gelation with combination with the (B) component and the (C) component (meta). In addition, the thing of the above-mentioned range of the (D) component for which small quantity is used comparatively is also the description. (D) There is an inclination for the branching reaction by chain transfer to increase and to cause gelation as a component increases.

[0023] moreover -- the case where the (E) component is used -- the total mol sum of (A) - (E) component -- receiving -- usually -- or less about 40 mol % -- it is used less than [ 30 mol % ] preferably. (E) When a component exceeds 40-mol %, it is difficult to get in sufficient paper durability effectiveness. in addition -- the case where anionic is given to a copolymer as a (E) component -- said total mol sum -- receiving -- usually -- an anionic vinyl monomer -- 1 - 20-mol % -- desirable -- 2 - 15-mol % -- it is used. the case where cationicity is given to a copolymer -- the total mol sum -- receiving -- usually -- a cationic vinyl monomer -- 1-20-mol % -- desirable -- 2-15-mol % -- it is used. moreover -- the case where both sexes are given to a copolymer -- the total mol sum -- receiving -- usually -- an anionic vinyl monomer -- 1-15-mol % -- desirable -- a 2-10-mol % and cationic vinyl monomer -- 1-15-mol % -- desirable -- 2-10-mol % -- it is used.

[0024] Composition of the copolymer used for this invention can be conventionally performed by various well-known approaches. For example, said various monomers ((A) - (D) component or (A) - (E) component) and water can be taught to a predetermined reaction container, a radical polymerization initiator can be added, and the water-soluble acrylamide (meta) system copolymer made into the purpose by warming under churning can be obtained. Reaction temperature is about

50-100 degrees C, and reaction time is usually about 1 - 5 hours. Reaction concentration (monomer concentration) can usually be performed at about 10 - 40 % of the weight, and can carry out a polymerization also in high concentration. Moreover, without diluting also in a high-concentration case, it can be used and the water solution of the obtained copolymer can be saved. In addition, an approach to teach a monomer can be performed by the various approaches that a coincidence polymerization, a continuation dropping polymerization, etc. are conventionally well-known. As a radical polymerization initiator, the usual radical polymerization initiators, such as a redox system polymerization initiator of the form which combined persulfate, such as potassium persulfate and ammonium persulfate, or these and the reducing agent like a sodium hydrogensulfite, can be used. Moreover, an azo system initiator may be used together to said radical polymerization initiator. the amount of the radical polymerization initiator used -- 0.05- of the AUW sum of a monomer -- it is 0.1 - 0.5 % of the weight preferably 2.0% of the weight. At 0.05 % of the weight, when the polymerization itself does not fully advance but it exceeds 2.0 % of the weight of another side, it is difficult to obtain the amount polymer of macromolecules.

[0025] Weight average molecular weight is 500,000 to about 6 million, and can usually use the acrylamide (meta) system copolymer obtained in this way as various kinds of additives for paper manufacture, such as a layer indirect adhesive of externally adding chemicals, such as internal chemicals, such as a filtration improvement agent and a paper reinforcing agent, and a surface paper reinforcing agent, and \*\*\*\* doubling paper. In addition, when using as a layer indirect adhesive of internal chemicals, such as a filtration improvement agent and a paper reinforcing agent, and \*\*\*\* doubling paper etc., it is desirable that weight average molecular weight is 2 million or more. Moreover, viscosity is good to usually use about (25 degrees C) 10000cps by the following descriptions from the point of handling nature. In addition, although the additive for paper manufacture of this invention is adjusted to 10 - 40 % of the weight of solid content concentration, it can adjust about (25 degrees C) 10000cps of viscosity for solid content concentration to 40% of the weight of a case below. Usually, it is desirable to make solid content concentration into 30 or less % of the weight. Thus, although the additive for paper manufacture which comes to contain the acrylamide (meta) system copolymer of this invention is the amount of macromolecules, it is hypoviscosity and can be used by high solid content concentration.

[0026]

[Effect of the Invention] Although the additive for paper manufacture of this invention contains the acrylamide (meta) system copolymer of the amount of (1) macromolecules, it is hypoviscosity comparatively and excellent also in workability. Moreover, transportation cost is sharply reducible, while high-concentration-izing of product concentration is possible and being able to improve productivity. Moreover, it can guess that the acrylamide system copolymer (2) Obtained (meta) is high branching structure, and the contact between pulp fiber shows many various characteristic engine performance as additives for paper manufacture, such as a paper durability enhancing effect. Many effectiveness which was excellent also in the bottom of the latest severe paper-making conditions as the result as various kinds of additives for paper manufacture, such as a layer indirect adhesive of externally adding chemicals, such as internal chemicals, such as a filtration improvement agent and a paper reinforcing agent, and a surface paper reinforcing agent, and \*\*\*\* doubling paper, is done so.

[0027]

[Example] Hereafter, an example and the example of a comparison are given and this invention is explained more concretely. In addition, each of sections and %s is based on weight criteria, as long as there is no special mention.

[0028] The acrylamide 234.6 section (it is the same as that below of 94.97 below [ % and ] to the total mol sum of a monomer), the meta-allyl compound sulfonic-acid soda 16.5 section (three-mol %), the dimethyl acrylamide 6.9 section (two-mol %), the triallyl isocyanurate 0.074 section (0.03-mol %), and the ion-exchange-water 960 section (21% of monomer concentration) were taught to the 4 opening flask equipped with example 1 agitator, a thermometer, a reflux cooling pipe, and nitrogen gas installation tubing, and the oxygen in the system of reaction be removed through nitrogen gas. The inside of a system was made into 40 degrees C, and the ammonium persulfate 0.25 section and the sodium-hydrogensulfite 0.15 section were supplied as a polymerization initiator to the bottom of

churning. It was kept warm for 2 hours, after carrying out a temperature up to 90 degrees C. The ion-exchange-water 70 section (it adjusts to 20% of solid content concentration) was supplied after polymerization termination, pH4.5, 20.2% of solid content, and viscosity (25 degrees C) obtained 9800cps, and weight average molecular weight obtained the copolymer water solution of 2,900,000. Moreover, it was 0% when the amount of gels was measured. In addition, although the amount of gels does not pass this filter when filtering a sample with a 0.45-micrometer membrane filter, it means a content (% of the weight).

[0029] In examples 2-7 and one to example of comparison 4 example 1, as shown in Table 1, even if few [ either ] among the class of (A) - (E) component, or its operating rate, one sort was changed, and also the same actuation as an example 1 was performed, and various copolymer water solutions were obtained. the description of the obtained various copolymer water solutions -- a value is shown in Table 2.

[0030]

[Table 1]

	モノマーの種類および使用割合（モル%）						
	(A) 成分	(B) 成分	(C) 成分	(D) 成分	(E) 成分		
					アニオン	カチオン	ニオン
実施例 1	AM 94.97	SMAS 3	DMAA 2	TAIC 0.03	--	--	--
実施例 2	AM 89.97	SMAS 3	DMAA 2	TAIC 0.03	AA 5	--	--
実施例 3	AM 89.97	SMAS 3	DMAA 2	TAIC 0.03	--	DM 5	--
実施例 4	AM 88.97	SMAS 3	DMAA 2	TAIC 0.03	AA 3	DM 3	--
実施例 5	AM 84.97	SMAS 3	DMAA 2	TAIC 0.03	--	--	AN10
実施例 6	AM 88.97	SMAS 3	IPAA 2	TAIC 0.03	AA 3	DM 3	--
実施例 7	AM 88.97	SAAS 3	DMAA 2	TAF 0.03	AA 3	DM 3	--
比較例 1	AM 90.80	SMAS 3	---	TAIC 0.20	AA 3	DM 3	--
比較例 2	AM 90.80	SMAS 3	---	TAF 0.20	AA 3	DM 3	--
比較例 3	AM 90.97	SMAS 3	---	TAIC 0.03	AA 3	DM 3	--
比較例 4	AM 91.97	---	DMAA 2	TAIC 0.03	AA 3	DM 3	--

[0031] front Naka, AM:acrylamide, SMAS:meta-allyl compound sulfonic-acid soda, DMAA:N,N-dimethylacrylamide, IPAA:N-isopropyl acrylamide, TAIC:triallyl isocyanurate, and TAF: -- 1, 3, 5-thoria chestnut roil hexahydro-S-triazine, AA:acrylic acid, DM:dimethylaminoethyl methacrylate, and AN:acrylonitrile are expressed.

[0032]

[Table 2]

	性 状				
	pH	固形分 (%)	粘度 (c p s)	重量平均分子量	ゲル量 (%)
実施例 1	4. 3	20. 8	9950	$300 \times 10^4$	0
実施例 2	4. 3	20. 5	9300	$280 \times 10^4$	0
実施例 3	4. 6	20. 4	8900	$305 \times 10^4$	0
実施例 4	4. 2	20. 5	9500	$290 \times 10^4$	0
実施例 5	4. 3	20. 8	9900	$280 \times 10^4$	0
実施例 6	4. 5	20. 2	9100	$295 \times 10^4$	0
実施例 7	4. 6	20. 5	9300	$275 \times 10^4$	0
比較例 1	4. 6	20. 4	11200	$260 \times 10^4$	15
比較例 2	4. 5	20. 6	12300	$250 \times 10^4$	20
比較例 3	4. 5	20. 3	4100	$115 \times 10^4$	0
比較例 4	4. 4	20. 1	9000	$85 \times 10^4$	10

[0033] Beating is carried out with a beater. (The performance-evaluation approach 1) corrugated paper used paper -- a Niagara style -- Add a sulfuric-acid band 1.6% to the pulp adjusted to Canadian standard freeness (C. S.F) 420ml, and it is referred to as pH5.5. Subsequently, 0.6% for pulp is added by making into a paper reinforcing agent each copolymer water solution obtained in examples 1-11 or the examples 1-5 of a comparison. After agitating, pulp slurry concentration is diluted so that it may become 0.1%, and it is basis-weight 150 g/m<sup>2</sup> with the TAPPI sheet machine. Paper making is carried out so that it may become, and it is 2.5kg/cm. Press dehydration was carried out for 2 minutes. after [ subsequently, / JIS ] drying for 3 minutes in 105 degrees C with a rotation mold dryer and carrying out gas conditioning to the bottom of the condition of 20 degrees C and 65%R.H. for 24 hours P 8112 -- applying correspondingly -- a ratio -- bursting strength was measured. A result is shown in Table 3.

[0034] (The performance-evaluation approach 2) N-BKP -- a Niagara style -- each copolymer water solution obtained in each above-mentioned example and the example of a comparison by the pulp (pH6.8) which carried out beating with the beater, and which was adjusted to 550 (C. S.F)ml -- the above -- the same -- adding -- the same actuation as the above -- carrying out -- a ratio -- bursting strength was measured. A result is shown in Table 3.

[0035]

[Table 3]

	評価方法 1	評価方法 2
実施例 1	2. 6 2	5. 6 7
実施例 2	2. 6 8	5. 7 6
実施例 3	2. 7 3	5. 8 8
実施例 4	2. 7 2	5. 8 5
実施例 5	2. 6 0	5. 7 4
実施例 6	2. 6 5	5. 7 5
実施例 7	2. 6 7	5. 7 7
比較例 1	2. 4 2	5. 5 1
比較例 2	2. 4 5	5. 4 8
比較例 3	2. 3 8	5. 2 5
比較例 4	2. 3 5	5. 2 2

[0036] From the result of Table 3, it is admited that the additive for paper manufacture using the acrylamide system copolymer obtained by this invention discovers the outstanding paper durability enhancing effect.

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[Translation done.]